I. STUDIES OF ZEEMAN EFFECTS FROM SOLUTIONS OF EUROPIUM AND NEODYMIUM SALTS

II. THE EFFECT OF ELECTROLYTES ON THE SOLUBILITY AND ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE IN WATER

BY

GEORGE JULIAN ROTARIU

B.S., University of Chicago, 1939
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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. STUDIES OF ZEEMAN EFFECTS FROM SOLUTIONS OF EUROPIUM AND NEODYMIUM SALTS

Introduction

The effect of a high magnetic field on solutions of salts of trivalent europium and neodymium was investigated spectrographically in the hope of checking the J-values of the energy levels between which the absorptions occur, and arriving at an understanding of the symmetry of arrangement of ions in solutions.

Gobrecht (1) had interpreted the spectra of the trivalent europium ion in crystals at 4650A as due to a $J = 0$ to $J = 3$ transition. This was partially checked for crystals by Schmillan (2), and for solutions by Freed and coworkers (3). That the spectra of europium in solutions can be used to describe the symmetry of arrangement of other ions about the europium ion has been demonstrated by Freed (4).

Results

The absorption spectra of solutions of various salts of europium and neodymium were obtained with the use of a Hilger spectrograph (dispersion of 2.22A per mm. at 4650A) and an electromagnet which achieved a magnetic field of 31,000 gauss. Transverse Zeeman effects only were sought. A 1.2 molar solution of europic nitrate did not exhibit a Zeeman effect at 4650A. However, a 0.233 molar solution of this compound in absolute ethyl alcohol did reveal such an effect in the 4658A component at room temperature. A lowering of the temperature to — 80°C caused the original doublet to change into a triplet (no field) : this indicated a change in structure of the alcohol about the europic ion which possessed less symmetry than previously. At — 22°C and at — 80°C, the

spectra of this solution, both with and without the field of 31,000 gauss, seemed to reveal a fine structure in each of the three components (4648A, 4652A, 4658A). This would indicate a lower symmetry in the alcohol at these temperatures than suspected.

A 1:1 aqueous mixture of 0.466 molar europic nitrate and 0.466 molar ethylenediamine tetracetate revealed an absorption spectrum with only one line at 4652A (1.6A wide) and no lines at 5250A. No definite statement concerning the symmetry of this europium complex can be made, although if the same selection rules for the transitions hold, the symmetry indicated is very high. No effect of the field of 31,000 gauss was noted on this mixture.

The spectra of a 0.466 molar aqueous solution of neodymium nitrate, investigated in the region of 5300-6300A, revealed two sharp lines at 6256A and 6222A. A solution of 4/3 mole ratio of neodymium-ethylenediamine tetracetate in water exhibited a spectrum with lines at 6270A, 6252A (?), 6235A, and at 6222A. A 1:1 aqueous mixture of 0.466 molar neodymium nitrate and 0.466 molar ethylenediamine tetracetate revealed a spectrum which resembled that of the 4/3 complex in intensity, with lines at 6274A and at 6230A (?). No effect of the field of 31,000 gauss was noted in the spectra of these neodymium solutions. The main band at 5770A (200-300A wide) for the neodymium ion seemed unaffected by the complexing and by the influence of the high magnetic field.

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II. THE EFFECT OF ELECTROLYTES ON THE SOLUBILITY AND ULTRAVIOLET ABSORPTION SPECTRA OF BENZENE IN WATER

Introduction

Certain metal ions and non-metals have been shown to act as electron acceptors with double bonds (1) and aromatic rings (2, 3.) The lack of spectral evidence for the existence of these complexes, as well as the lack of solubility information in this field, prompted this study.

Results

The spectral investigation was carried out with aqueous solutions of various metal salts (benzene saturated) in the region 2000A to 3450A with the aid of the Cary Recording Spectrophotometer. Spectra of the solutions, with and without benzene dissolved, are reproduced for silver nitrate, silver perchlorate, silver sulfate, silver ammonium chloride, mercuric chloride, cuprous chloride, zinc chloride, hydrochloric acid, sodium hydroxide, ammonium hydroxide, and sodium chloride. The spectra for aqueous hydrochloric acid solutions saturated with benzoic acid and for n-heptane solutions of iodine with aniline and biphenyl are also shown.

Solubility determinations were made of benzene in aqueous solutions of 0.1 molar and one molar hydrochloric acid, sodium hydroxide, ammonium hydroxide, and sodium chloride at 0.15°C, 20.00°C, and at 29.80°C. The apparatus and technique has been described by Bohon (4).

The only change noted in the ultraviolet absorption spectra was in the benzene band at 2100A. This is an N - V transition, and its intensity was markedly increased by solutions of hydrogen chloride, zinc chloride, silver perchlorate and by water itself, even though the solubility of benzene was decreased in

the cases of hydrogen chloride and silver nitrate (4). The addition of sodium hydroxide greatly reduced the intensity of the 2100A band: this was accompanied by a decrease in solubility. Despite the intensity changes produced in the 2100A band, the main band at 2535A remained unaffected for all of the solutions. Consideration of this data leads to the conclusion that the hydrogen ion is interacting with the benzene ring, possibly to form a complex, and is believed to do so through a polarizing action on the benzene ring as evidenced by the enhancement of the 2100A band. It is possible that complex formation of other positive ions with the benzene ring might be indicated likewise.

The interpretation of the complex formation between iodine and benzene as an acid-base reaction is reasonable, since auxochromic groups increase the tendency of the benzene ring to act as an electron donor, and negative groups, as biphenyl, decrease it. In the case of the silver ion complex, the behavior is reversed in that the biphenyl shows a greater tendency to form a complex, and a simple interpretation of the reaction as due to the basic character cannot be justified.

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VITA

The author was born in Los Angeles, California, on August 24, 1917. He attended Waller High School (Chicago) and graduated in 1934. He graduated from Wright Junior College (Chicago) with honors in 1936, and received the B. S. degree (1939), and the M. S. degree (1940) at the University of Chicago. The author was engaged in war research at the Toxicity Laboratory at the University of Chicago from 1941 to 1945, during which time thirteen restricted publications were written. The year, 1945-1946, was spent as Research Chemist with Lever Brothers (Chicago). From 1946 to 1948, the author was an Instructor in the Physical Sciences (College) at the University of Chicago. He enrolled in the Graduate College at the University in the fall of 1948, and has since held a half-time teaching assistantship in the Physical Chemistry Department.